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A Comprehensive Review of Biomass Pyrolysis as a Process of Renewable Energy Generation

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Abstract
Energy is considered the basis for the progress and prosperity of nations and societies. It is also the cornerstone of economic and social development. The limited availability of fossil fuels and the growing awareness of the detrimental environmental consequences resulting from greenhouse gas emissions have reinforced the importance of biomass as an energy resource in developed and developing countries. This review presents the summary of biomass for energy generation, the fundamental principles and application of biomass pyrolysis as well as some of the factors that can affect pyrolysis of biomass to produce bio-fuel. Some of the factors examined were biomass type, types of pyrolysis as well as pyrolysis conditions such as temperature and particle size. Other factors examined were retention time, biomass moisture content and the use of catalyst. Also included in the clusters were heating rate and the pyrolysis environment. The study concluded that most biomass residues lend themselves easily to process of pyrolysis and all the factors and variables examined in one way or the other had effects on biomass pyrolysis and there exists optimum or threshold value for each feedstock depending on the operating conditions
Keywords: Biomass, bio-fuel, char, chemical composition, energy, factor, pyrolysis

1. Introduction

Energy is an important factor, if not the most critical factor in developmental activities of any nation. The measure of level of social-economic growth and standard of living of the people of any nation are largely energy dependent (El-Saeidy, 2004; Agbontalor, 2007). The growing world population, industrialization, technological advancement and transportation had brought energy demand under an increased pressure. The world's energy markets rely heavily on the fossil derived fuels whose reserves are finite (Agbontalor, 2007). Currently, 85% of the world's energy demand is met by combustion of fossil fuels which are depletable. Furthermore, the global energy demand is expected to grow by about 50% by 2025, the major part of this increase coming from rapidly emerging countries (Agbro and Ogie, 2012). Therefore, there is the urgent need to generate alternative source of energy, which must not only be renewable, but must not pose any hazard to both humans and ecology (Oladeji, 2012a). In this regards, agricultural residues in form of biomass can play a significant role in biomass energy generation (Titiladunayo, 2002; Oladeji, 2011a). The aim of this study was to make comprehensive review on biomass pyrolysis. In addition, those factors that have effects on the production of bio-fuels through the pyrolysis of biomass residues were examined.

2. Methodology

The method adopted for the study involved extensive literature review on the subject matter. Sources used included internet, previous reports and publications of notable researchers (the present lead and correspondence author inclusive) on biomass, particularly on pyrolysis of agricultural and animal residues.

3. Biomass

Biomass can generally be defined as any hydrocarbon material which mainly consists of carbon, hydrogen, and nitrogen. Sulphur is also present in less proportion. Some biomass types also carry significant proportion of inorganic species. The concentration of the ash arising from these organics changes from less than 1% in softwoods to 155 in herbaceous biomass and agricultural residues (Yaman, 2004). Biomass resources include various natural and derived materials, such as woody and herbaceous species, wood wastes, bagasse, agricultural and industrial residues (Agbro and Ogie, 2012). Others are waste paper, municipal solid waste, sawdust, bio-solids, grass, and waste from food processing. Also in the cluster are animal wastes, aquatic plants and algae and so on (Oladeji, 2011b).

3.1 Advantages of Biomass for Energy Production

There are a lot of benefits to be derived from using biomass for energy production. Among these benefits are:
i. They are readily available in the rural areas, where petroleum products are not always available and affordable.
ii. Their application for energy generation serves as a useful way of waste disposal.
iii. Their use will help to reduce rate of deforestation as the rate of felling of trees in the forest will be greatly reduced (Adekoya, 1989).
iv. Their use will promote clean environment as less pollutants are deposited into the atmosphere, thereby

reducing the green house effect (Wilaipon, 2009).
v. Their use will serve as additional way of generating income to farmers in rural areas, because once a market has been established, the residues may as well acquire a monetary value (Oladeji, 2011b).

3.2 Limitations of Raw Biomass as Alternative Fuel

It is observed that several kinds of agricultural residues and animal wastes are available and ready to be utilized as fuels. Utilization of these residues is often difficult due to their uneven characteristics. This is because, it is widely accepted that the majority of the residues are not appropriate to be used as fuels directly. As compared to other kinds of fuels, biomass residues have lower density, higher moisture content and lower energy density. Besides, the low bulk density and dusty characteristics of the biomass, there are also problems that are associated with their transportation, handling and storage (Husan, et al, 2002). Therefore, there is the need to transform these residues into forms that will make their combustion easy and more efficient.

4. Pyrolysis Process

According to Agbontalor (20071), there are many conversion routes of turning biomass into renewable form of energy, one of which notable ones is pyrolysis. Pyrolysis belongs to a thermo-chemical process. Pyrolysis of biomass can be described as the as direct thermal decomposition of the organic matrix in the absence of oxygen to obtain an array of solid, liquid and gas products (Girard, et al., 2005; Pro-Natural International, 2004).
Pyrolysis as a thermo-chemical process has long been employed in the breakdown of organic materials into chemical and energy products (Fapetu, 2000a; Bridgewater, 2002; Chopra and Jain, 2007; Demirbas, 2009).

5. History of Pyrolysis

The history of pyrolysis dated back to late 1990s in the United States of America when the problems related to dioxin motivated incinerator manufacturers to develop pyrolysis process for handling municipal solid wastes with moisture contents of 30 to 70% (Czernik and Bridgewater, 2004). In developing countries, most pyrolysis processes are carried out in piles, earth mound and pit kilns with the sole aim of producing charcoal of low quality (Bamigboye and Oniya, 2003)

6. Types of Pyrolysis

Pyrolysis technologies can be broadly categorized into three groups (Bridgewater, 2003; Putun, 2002). These are slow and fast pyrolysis. Slow pyrolysis is characterized by slow biomass heating rates, low temperature and lengthy time of producing gas and solids, while fast pyrolysis takes place in less than five seconds and within temperatures between 300^0C and 550^0C (Bridgewater and Peacocke, 2000).

7. Agricultural and Animal Residues that had been subjected to Pyrolysis

Many agricultural residues and animal wastes had been subjected to process of pyrolysis by different researchers. Notable among these biomass residues are corn cob (Bamigboye and Oniya, 2003), maize (Encinar, et al., 1997), *Euphorbia rigida* (Ozcan, et. al., 2000), wood waste (Fapetu, 2000b), cow dung (Oladeji, 2011c), melon shells (Oladeji, 2012b), palm kernel shells (Weerachanchai, et al, 2011), cotton straw and stalk (Putun, 2002; Chen, et al., 2003a) as well as cassava pulp residue (Weerachanchai, et al, 2011). Also included in the cluster are rice straw and pine sawdust (Chen, et al., 2003a.), poultry litter (Oladeji, 2012b), tobacco residue (Putun, et al., 2007) and cotton gin (Aquino, et al., 2007)

8. Advantages of Pyrolysis

Pyrolysis process offers the following advantages among others:-
i. Since pyrolysis takes place in oxygen free environment, there is no or fewer air emissions and this is beneficial to both human and ecology (Eunomia Research and Consulting, 2008).
ii. The pyrolysis plants are modular. They are made up of small units, which can be added to or taken as waste streams or volumes change (e.g. with increased recycling) and are therefore more flexible and can operate at a smaller scale than mass burn incinerators (Eunomia Research and Consulting, 2008).
iii. Pyrolysis plants are quicker to build and set up
iv. Pyrolysis processes produce more useful products than standard incineration. This is because; gases, oils and solid char obtained from the process can be used as bio-fuels or purified as a feedstock

9. Products of Pyrolysis

There are three major products of pyrolysis of biomass residues. These are the char, the bio-oil and pyrolytic gas. All these are discussed in section 9.1 to 9.3

9.1 Char Product

This is solid product of pyrolysis. It is usually characterized for bulk density, proximate analysis which includes moisture, volatile, ash contents and fixed carbon contents. Further characterization includes elemental analysis (carbon, hydrogen, oxygen and nitrogen), energy value (low and high heating values) and porous properties (Nugranad, 1997). All these characteristics are usually determined through various American Standards for Testing Materials (ASTM)

9.2 Liquid Product

This is usually the bio-oil obtained from the process of pyrolysis. It is usually analyzed for its physicochemical properties (Biomass Technology Group, 2003). The oils have eating values of 40-50% of that of hydrocarbon fuels (Yaman, 2004). However, it must be noted that some problems may occur in the combustion systems when these liquids are burnt raw without upgrading. This because they have very high water content and this is detrimental for ignition. Moreover, organic acids in the oils are highly corrosive to common construction materials. Sometimes, solid may be in the liquids and this may block injectors or corrode turbine blades. However, the organic acid in the bio-oil can be separated through fractional distillation (Bamigboye and Oniya, 2003). Beside, over time, the reactivity of some components in the oil may lead to formation of larger molecule resulting in high viscosity and in slower combustion (Oasman and Czernik, 1999).

9.3 Gas Products

This is also known as pyrogases or syngases. They were usually identified and quantified by gas chromatograph with a thermal conductivity detector. Some of the gases that can be identified are CO_2, H_2, O_2, N_2, CO, CH_4 and son depending on the composition of original biomass feed stocks (Oladeji, 2012b).

10. Applications of Products of Pyrolysis

The main products of pyrolysis are char, bio-oil and pyrogas. Each of these products has got its specific application. For example the char products obtained could be used for traditional and industrial cottage applications as in domestic cooking and as fuel in open earth furnace for blacksmithing and goldsmithing operations (Fapetu, 2000a and b). The bio-oil can be used in internal combustion engine (Bridgewater and Peacocke, 2000; Biomass Technology Group, 2003), while the pyrolytic gas could be used as household cooking gas and as fuel for gas lamps (Bamigboye and Oniya, 2003; Bridgewater, 2002). The pyrogas can be collected and used as a supplemental fuel for heating the pyrolysis reactor. Furthermore, numerous other applications are available for gases from biomass pyrolysis. Findings show that pyrolysis gas compared with conventional gasification gas is more advantageous, as it is higher in heating value and consequently can be applied in gas turbine or other combustion engines for power generation (Chen, et al., 2003a and b). Apart from the usage highlighted as fuels, the products of pyrolysis can be used in particular fields. For instance, the pyrolytic char usually has a porous structure and a surface area that is appropriate to use as active carbon (Yaman, 2004). The liquids obtained from pyrolysis contain many chemical compounds that can be used as feedstock for synthesis of fine chemicals, adhesives, fertilizers and so on (Meir and Faix, 1999). In ancient Egypt, the chemical products obtained from pyrolysis had been used for preservation of dead bodies (Czernik and Bridgewater, 2004).

11. Factors Affecting Pyrolysis of Biomass

The quantity and quality of products of pyrolysis of biomass depend on a number of factors (Weerachanchai, et al, 2011). Generally, the product yields will include a solid carbon- rich residue in form of charcoal and a range of volatile products, which include condensable and non-condensable. The yields depend essentially on both the physical and chemical characteristics of the biomass (feed stocks) as well as specific pyrolysis conditions, which include particle size, temperature, pressure, retention time, heating rate, surrounding atmosphere as well as mineral compositions of the biomass feed stocks (Oladeji, 2012c). Chemical structure of biomass is also included in the cluster (Yaman, 2004). The variation of pyrolytic conditions can lead to increase in some of the products of pyrolysis; while at the same time can decrease the other pyrolytic products. The effects of these operating and processing conditions are very important as they can help in the development of pyrolysis models (Zanzi, et al., 2002). Some of factors that can affect products of pyrolysis are discussed in sections 11.1-11.8

11.1 Pyrolysis Temperature

The temperature at which biomass material is pyrolyzed is very important and the final temperature is one of the major determinants in the thermal process. For example, at low temperatures below 150^0C, tar formation usually does not take place. However, as temperature increases, formation of char begins to take place, which in turn results in higher yields of gaseous products and lower yields of char. This is due to greater decomposition of the biomass and this also leads to decrease in liquid products resulting in increase in gas production apparently due to devolatilization of the cellulosic and hemi-cellulosic materials (Aquino, et al., 2007; Putun., et al., 2005; Fapetu, 1994).

Weerachanchai, et al, 2011 studied the effects of pyrolysis temperature on the product yields of palm kernel cake and cassava pulp residue and noted that the char yield decreased sharply from 300 to 500 ^{0}C followed by a slow decrease at higher temperatures and approaching a constant value at 800 ^{0}C. Temperature is also found to have an influence on the composition of element in the products. For example, studies by few researchers (Zanzi, et. al. 2002; Della Rocca, et. al. 1999) showed that carbon content increases with an increase in temperature, while the hydrogen and oxygen contents decrease.

11.2 Types of Biomass Feed Stocks

There are great variations in the physical and chemical structure and composition of different biomass materials. For examples, hardwoods produce lower char yields than soft woods, while agricultural crop residues produce more char and less gas yields than woods.

Fapetu (1994) in his work on Ekki wood (hard wood), coconut and palm kernel shells obtained char yield of 25.07% by weight for Ekki wood, while coconut and palm kernel shells yielded 29.62 and 28.64% by weight respectively of the oven-dried weight of feedstock. This result agrees with the findings that wood materials generally yield lower chars than crop residues. Zanzi et al (2002) subjected wood, olive waste and wheat straw to rapid pyrolysis. Their findings showed that wood gave more volatile yield and less char than both agricultural residues. They attributed the higher char yield for the agricultural residues to the presence of large amount often associated with residues which favours the charring reaction. Their findings also showed higher yield for olive waste compared to wheat straw and this was attributed to more lignin content in the olive waste. Sections or parts of the feedstock plant being pyrolyzed were also studied by Fapetu (1994) and it was discovered that there are even variations within the same species of biomass. For example when the mesocarp and the endocarp of babassu nut were subjected to pyrolysis, the mesocarp yielded by weights 32.24% char and 21.23% pyrogas, whereas the endocarp yielded 32.32% and 19.22% by weights of char and gas respectively. The results furthered revealed that the yields of pyroligneous liquor were 47.85% and 45.53% by weights for mesocarp and endocarp of the nut respectively (Fapetu, 1994). The author, Oladeji (2013) in an experiment to characterise products of pyrolysis between cow dung and poultry obtained 44.2 wt% and 47.3 wt% for char yields respectively, while the values of bio-oil yields are 37.54 wt% and28.33 wt% for cow-dung and poultry litter respectively. For pyrogas, cow dung yielded 18.25 wt%, while the poultry yielded 24.3 wt%. The constituents of pyrogas for cow dung are 74.78% carbon and 25.22% hydrogen, while for poultry litter; it was 65.24% carbon and 34.76% hydrogen. Further chemical analysis revealed that that the pyrogas of cow dung contained two different gases i.e 56.67% by volume of methane (CH_4), 54.33% by volume of propane (C_3H_8), while for poultry litter, the pyrogas is made of four constituent gases, which are 22.89% by volume of methane (CH_4), 17.35% by volume of propane (C_3H_8), 35.22% by volume of ethyne (C_2H_2) and 24.54% by volume of ethane (C_2H_8). The inference that could be drawn from the above stated results is the product and percentage yields as well as constituents depend on the type of the biomass residue used. It can also be concluded that some biomass residues lent themselves easily to process of pyrolysis than others.

11.3 Heating Rate

The product yields of pyrolysis including char, liquid and gas to certain extent depends on the applied heating rate. For example, in their work on effect of heating rate on product yields of palm kernel cake and cassava pulp residue, Weerachanchai, et al, 2011 noted that heating rate in the range of 5-20^{0}C/min and within the pyrolysis temperature of 700^{0}C had no significant effect on the product yields of pyrolysis over the relatively narrow range from 5-20^{0}C/min. The result of their findings agreed with the work of Putun et al, (2007), which showed that that pyrolysis study at temperature from 500 - 700^{0}C had no important effect of heating rate on product yields in the range of 7 – 40^{0}C. However, the work of Karaosmanoglu et al. (1999) indicated that heating rate higher than 30^{0}C/min provided higher yields of liquids and gas products and lower char yield than those derived from pyrolysis at 10^{0}C.

11.4 Particle Size

The specific surface area of particles or pieces undergoing pyrolytic process has considerable influence on the efficiency of thermo-chemical conversion and the reaction time (Zabaniotou and Karabelas, 1999). It has been established that particle size has an influence on the products yield and composition. This is conclusion by Zanzi et al (2002) in their work on the rapid pyrolysis of wood and agricultural residues in a free fall reactor. A decrease in the char yield and an increase of the gas yield were obtained when smaller particles of wood and olive waste were pyrolyzed. In a similar experiment conducted by Zanzi et al (2002), it was found that the char yield after total pyrolysis was higher in pyrolysis of pelletized wheat straw than in untreated straw. The effect of particle size in the range of 0.71 – 3.56 mm on product yields at 700^{0}C was studied by Weerachanchai, et al. (2011) using palm kernel and cassava pulp residues. Their results showed that the pyrolysis of the two biomasses with the average of 2.03 mm gave the maximum in the liquid yield of 54.3 wt% and 42.4 wt% for palm kernel cake and cassava pulp residue, respectively. Their study further revealed that for particle sizes smaller than 2.03 mm, higher gas and char yields but a lowering in liquid yield were obtained as the particle size was decreased. Their study suggested that it is likely that the smaller size of biomass particles could affect greater heat transfer because of less temperature inside the particle, thus giving higher yields of released gases and volatiles. In addition, the denser packing of smaller size particles could impede the flow of sweeping gas. This would consequently prolong pyrolysis products to stay in the reaction zone, thus allowing secondary reactions via thermal cracking, re-polymerization, and re-condensation to occur, thereby giving additional decomposition of higher molecular weight volatiles to gas product with reduction in the amount of liquid product and increased formation of solid char. For particle sizes larger than 2.03 mm, Weerachanchai, et al. (2011) noted that the variation in product yields was not so sensitive to the change in particle size, with slight decreasing of liquid product and small increasing of gas and char products being observed for increasing in particle size. This was also observed by Guo and Lua (2001).

11.5 Retention Time

This is also known as residence time and this can be defined as the duration the pyrolysis products remain in the reactor chamber before they are discharged out of the reactor. According to Zanzi et al (2002), the residence time has an influence on products of pyrolysis. The increase in retention time may lead to the secondary reactions thereby resulting in secondary products. Aquino et al. (2007) varied the pyrolysis time during batch pyrolysis of cotton gin trash and it was discovered that char yield decreases slightly, why the gas yield increases with an increase in pyrolysis time. However, contrary results were obtained by Gan and Yuan (2008) which reported that increase in the retention time had no significant effect on gas yield during the hydrothermal pyrolysis of mixed crop residues. Their work further revealed that there was drastic effect on the char yield, which decreases with increase in retention time. The study also established optimal retention time for production of bio-oil. The oil yield was found to reach its maximum of 21wt% at 20 minutes retention time and then decrease when retention time was longer than 20 minutes.

11.6 The Use of Catalysts

Some catalyses have been used to improve the characteristics of pyrolysis products. In particular, oxygenates in the pyrolysis liquids can be reduced using zeolite type catalyses (Yamman, 2004). Putun et al. (2005) on pyrolysis of cotton seed cake using natural zeolite content as catalyst showed that increasing the zeolite resulted in a slight change in the pyrolysis conversion. Demirbas (2000) also noted that glycerol could be used as an organic solvent to improve conversion of biomass into bio-oil during pyrolysis. Addition of pyrolytic charcoal residues was found to promote rapid pyrolysis and save energy due to better microwave heating (Bridgewater and Peacocke, 2000; Yu et. al., 2006)

11.7 The Environment

The environment in which the process of pyrolysis takes place has been found to have influence on the product yields. Munir et al. (2009) studied the thermal characteristics of different biomasses under inert and oxidative environment. The result of their experiment showed diverse thermal behaviour on two conditions. It was discovered that the rate of weight loss and the reactivity of the biomasses in inert atmosphere were both less than in an oxidizing atmosphere. The result further showed that the rate of weight loss associated with oxidative degradation (air) almost doubled that for de-volatilisation under inert (N_2) condition.

11.8 Moisture Content

Moisture content can have different effects on pyrolysis product yields depending on the conditions (Antal and Gronli, 2003**).** In traditional charcoal kilns heated internally by wood combustion, high moisture levels lead to reduced charcoal yields as a greater quantity of wood must be burnt to dry and heat the feed. Increased moisture present when pyrolysis reactions are performed under pressure has been shown to systematically increase char yields (Antal and Gronli, 2003). As noted by Bridgewater and Peacocke (2000), fast pyrolysis processes in general require fairly dry feed, around 10% moisture, so that the rate of temperature rise is not restricted by evaporation of water. However, slow pyrolysis is more tolerant of moisture, the main issue being the effect on process energy requirement. For charcoal making, wood moisture contents of 15 – 20% are typical (Antal and Gronli, 2003).

Conclusion

From this review study, the following conclusions among others were drawn:-

- Pyrolysis belongs to a thermo-chemical process and can be described as the as direct thermal decomposition of the organic matter in the absence of oxygen to obtain three major products, which are char, bio-oil and pyrolytic gas.
- The quantity of three major products of pyrolysis depends mainly on the pyrolysis temperature and furthermore. Temperature is also found to have an influence on the composition of element in the products.
- Different biomass feed stocks lend themselves differently to process of pyrolysis.
- The product yields of pyrolysis including char, liquid and gas to certain extent depends on the applied heating rate.
- Particle size of the biomass feedstock has an influence on the products yield and composition.
- Catalyses can be used to improve the characteristics of pyrolysis products.
- The environment in which the process of pyrolysis takes place has been found to have influence on the product yields. The rate of weight loss and the reactivity of the biomasses in inert atmosphere were both less than in an oxidizing atmosphere.

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